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Irradiated polytetraflouroethylene (PTEF) and polyethylene (PE) microstructural changes studied by PAL technique

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Abstract Positron annihilation lifetime (PAL) technique has been employed to study the microstructural changes of PTFE and PE due to irradiation at low doses of neutrons (5-5.01) × 10^{-2} Gy. The size of the free volume holes and their fraction in PE and PTFE were determined from ortho-positronium lifetime component and its intensity in the measured lifetime spectra. The results show that this range of irradiation causes significant changes in the free volume hole sizes (V_h) and the fractional free volume (F_h), and thereby of PE and PTFE microstructure. The results can be explained by the viewpoint that the n doses induce degradation, cross-linking and crystallinity in PE and PTFE chains.

It has thus been shown that PAL can be an important microprobe to study the microstructure of the polymer in an atomic scale with an accuracy of about 4 picometer.

Keywords Positron annihilation, PE and PTFE, polymers, n-irradiation

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1. Introduction

Studies of the microstructure like free-volume properties at a molecular and atomic scale can provide a basic understanding of the mechanical and physical properties of polymers [1].

In PAL technique [2], one employs the positron emitted from a radioactive source as a probe to monitor the lifetime of the positron and positronium (Ps) (a bound atom consists of an electron and a positron) in the polymer material under study.

The positrons and the positronium atoms entering the polymer can be trapped in open spaces like holes, voids or cavities. The corresponding annihilation photons come from these open spaces. Positrons produced by the radioactive isotope of ^{22}Na are commonly used. The Ps atom formed can be in the singlet (p-Ps) or triplet state (o-Ps), with mean lifetime in free spaces of 0.125 ns and 140 ns, respectively.

In condensed medium, the mean lifetime of o-Ps is reduced to a few nanosecond [3] due to its interaction with surrounding molecules of the medium. So the results for o-Ps lifetime and its probability are related to free-volume hole size (V_h), fractional free volume (F_h) and distribution. The relation between the mean radius of free-volume hole size and the o-Ps lifetime $\tau_{\text{o-Ps}}$ was found according to the semi-empirical formula [4] :

$$\tau_{\text{o-Ps}} = 0.5\left[1 - R/R_0 + 0.159\sin\left(\frac{2\pi R}{R_0}\right)\right]^{-1} ns, \qquad (1)$$

where $R = R_0 + \Delta R$, ΔR is the electron layer thickness. The free-volume – hole size (V_h) is

$$V_h = \frac{4}{3}\pi R^3. \qquad (2)$$

The fractional free volume (the ratio of the free volume to the total volume) was found according to fitted empirical formula as [5] :

$$F_h = A V_h I_{\text{o-Ps}}, \qquad (3)$$

where A is a constant, its value is between 1 and 2 for polymers, V_h is the free-volume hole size and $I_{o\text{-}Ps}$ is the intensity of $\tau_{o\text{-}Ps}$.

PAL is widely used for investigating different aspects of polymer properties [6–11]. Positron and positronium lifetimes in polymer materials may be affected by different factors such as change in degree of crystallinity [12], blending of polymer [13,14], plasticization of polymer [15–17], aging of polymer [18,19], temperature [20–25], irradiation of polymer [26–41]. The present paper is to study the effect of n-irradiation on the microstructure of PTFE and PE, and to find a correlation between the irradiation dose and the changes in V_h and F_h values.

2. Experimental details and data analysis

The investigated PTFE samples of crystallinity of 75% and PE samples of crystallinity of (75–85)% were irradiated in air at room temperature by neutrons, using Am–Be neutron source. The samples were irradiated within the dose range (5–501)10^{-2} Gy, with a dose rate of 19×10^{-4} Gy/h. The positron lifetime measurements were performed using a fast-slow coincidence system (Figure 1), with a time resolution of 340 ps (FWHM). The positron source activity was

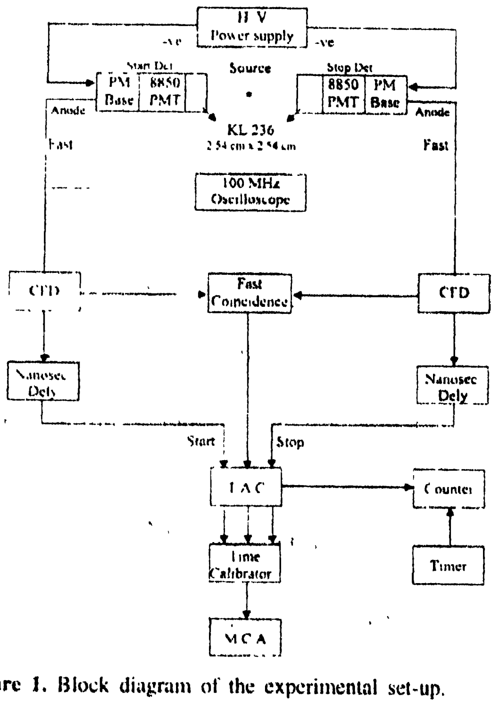

Figure 1. Block diagram of the experimental set-up.

12μCi, the fraction of positrons absorbed in the source was found to be 8%. The lifetime spectra were measured for each individual irradiation dose with a total integral of 2×10^6. The lifetime spectra were analyzed into three-lifetime components using PFPOSFIT program [42]. The free volume hole size, and the fractional free volume were calculated using eqs. 1, 2 and 3, respectively.

3. Results and discussion

The final analysis results for PTFE lifetime measurements of the spectra recorded at different n-irradiation doses are displayed in Table 1.

Table 1. Lifetime parameters for PTFE as a function of n-dose

Gy × 10^{-2}	t_3	err	I_3	err
0	2423	82	5.748	0 022
22.83	2772	98	5 913	0 021
36 38	2569	52	5.61232	0 033
59 28	2489	89	5.4	0 018
76.84	2470	44	5.999	0 01
108 79	2501	87	5 44	0 016
154.39	2209	78	5 92	0 039
201.21	2330	85	5.558	0 021
296.21	2260	88	5.647	0 048
501 03	2351	84	5 6565	0 018

The free-volume hole size and the fractional free volume hole sizes were plotted as a function of n-dose in Figures 2 and 3 respectively.

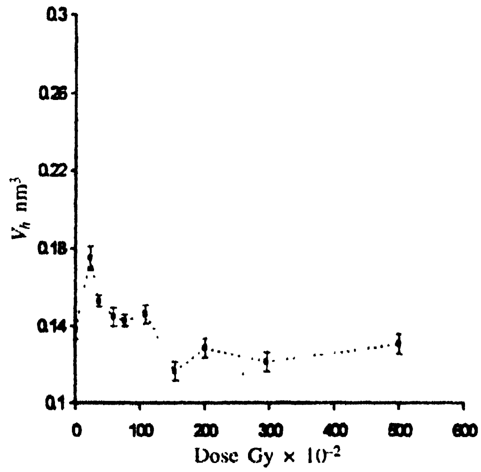

Figure 2. V_h for PTFE as a function of n-dose

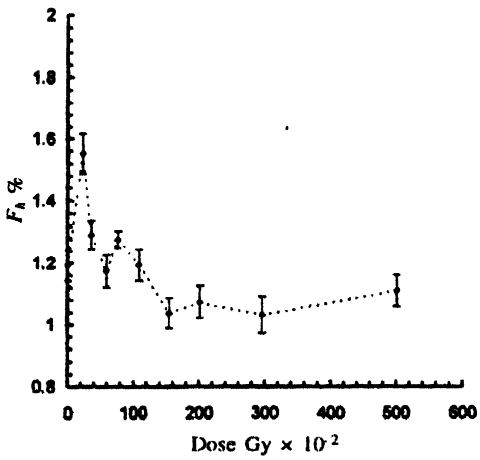

Figure 3. F_h for PTFE as a function of n-dose.

The V_h and F_h values for unirradated PTFE samples were found to be 0.1383 nm^3 and 1.192%, respectively. It is clear that V_h and F_h values increase with increasing n-dose up to a total n-dose of 22.83 × 10^{-2} Gy.

An increment of 26.58% and 30.23% are noticed in V_h and F_h values, respectively. This result suggests that n-dose induces degradation of PTFE chains, resulting in an increase of both the free-volume hole sizes and their number density. As shown in Figures 2 and 3, V_h and F_h values, decrease gradually with increasing dose (above 22.83) upto a total n-dose of 154.39 × 10^{-2} Gy, where their maximum increments are reduced to 10.93% and 8.3% respectively, at a total dose of 36.4 × 10^{-2} Gy, corresponding to percent reductions of 12.36 and 16.83 in V_h and F_h values respectively, relative to their values at 22.8 × 10^{-2} Gy. V_h and F_h reach their minimum values at 154.39 × 10^{-2} Gy n-total dose, where percent reductions of 15.52 and 12.9 respectively, are noticed in V_h and F_h values, corresponding to percent reductions of 33.3 and 33.14 respectively with respect to their maximum values (at 22.83 × 10^{-2} Gy dose).

These results indicate that the neutron dose above 22.83 × 10^{-2} Gy induces another process which is opposite to the degradation. This increases crystallinity in the amorphous regions of PTFE, resulting in reduction of degradation effect rate, thereby reducing both the inter-moleculai spaces, and their number density.

Increasing crystallinity in the amorphous sites reduces the free-volume hole sizes, and their number density (the regions where Ps atoms form and annihilate). The reduction of V_h and F_h is due to a combined effect of free radicals (induced as a result of n-irradiation) and increasing crystallinity.

Above n-dose of 154.39 × 10^{-2} Gy, V_h and F_h values begin to increase gradually with increasing n-dose upto a final total n-dose of 501.03 × 10^{-2} Gy, where their percent reductions are reduced to 5.3 and 6.8, respectively. Corresponding to increments of 12.1% and 7.03%, respectively with respect to their minimum values at 154.39 × 10^{-2} Gy, indicating the predominance of degradation or the degradation rate is higher than the rate of increasing crystallinity, Ps formation and annihilation are affected by chemical structure of polymer, crystallinity and quenching effect of free-radicals.

The positron and positronium lifetime spectra for unirradiated and n-irradiated PE samples were measured and analyzed using three lifetime components, V_h and F_h were calculated. The results are displayed in Table 2. The free volume hole size (V_h) and the fractional free volume F_h were plotted as a fraction of n-dose in Figures 2 and 3 respectively. The values of V_h and F_h for unirradiated samples are 0.1213 nm^3 and 1.011%, respectively. The initial n-dose in induces a percentage reduction of 0.326 or 6.44/Gy in V_h value and a percentage increment of 10.74 or 211 97/Gy in F_h value, indicating that n-dose results in increasing of cross-linking of PE and at the same time increasing, the number density of intermolecular spaces available for Ps formation. As the n-dose increases above 5.06654 × 10^{-2} Gy, V_h and F_h values increase and reach their maximum values of 0.126 for V_h (at 22.8 Gy-dose) and 1.1946% for F_h (at 13.85 Gy) corresponding to increments of 4.1% and 18.13% for V_h and F_h values respectively, suggesting the predominant of degradation of PE chains due to n-irradiation.

Table 2. Lifetime parameters for PE as a function of n-dose

Gy × 10^{-2}	τ_3	err	I_3	err
0	2254	50	5.56	0.16
5.07	2225	48	6.18	0.18
13.85	2258	68	6.56	0.31
22.83	2304	85	5.86	0.35
36.39	2111	79	6.64	0.27
59.28	2020	59	6.47	0.22
76.84	2186	72	5.83	0.24
108.79	2227	62	5.69	0.29
154.39	2258	59	6.14	0.25
201.20	2192	65	5.78	0.26
296.21	2237	69	5.40	0.28
501.03	2242	68	5.87	0.26

As the n-dose increases above 22.8 × 10^{-2} Gy, upto a total dose of 59.28 × 10^{-2} Gy, V_h and F_h values decrease gradually with increasing n-dose to reach their minimum values at 59.28 × 10^{-2} Gy n-total dose. The n-total dose (59.28 × 10^{-2} Gy) induces percent reductions of 18.61 and 5.31 in V_h and F_h values, respectively, corresponding to percentage reductions of 31.39/Gy and 8.96/Gy, respectively.

The corresponding percentage reduction relative to their maximum values are 21.82 and 29.85, respectively.

The reduction in V_h and F_h values is due to an increase of cross-linkings and crystallinity in the amorphous regions of PE, as a resultant effect of n-irradiation and the reaction of the reactive free radicals (induced as a result of n-dose effect).

Ps formation and annihilation is strongly affected by many factors such as three dimensional polymer structure, chemical structure, crystallinity, and free radicals. Neutrons-irradiation dose, produces free radicals in PE, as a results of interaction of fast neutrons and the capture of the thermal neutrons resulting in different chemical reactions, such as, recrystallization, creation of hydroperoxides, cross-linking, and degradation.

The oxygen dissolved in PE may be bound forming hydroperoxides at the polymer chains in the amorphous regions, causing the reduction of the amorphous regions, which is noticed as a decrease in V_h and F_h values. Above 59.28×10^{-2} n-total dose, V_h and F_h values increase with increasing dose upto n-total dose of 154×10^{-2} Gy, where percent increments of 23.26 and 16.92 is taken place in V_h and F_h values, respectively, relative to their minimum values, corresponding to an increase of 0.33% and 10.71%, respectively relative to their initial values.

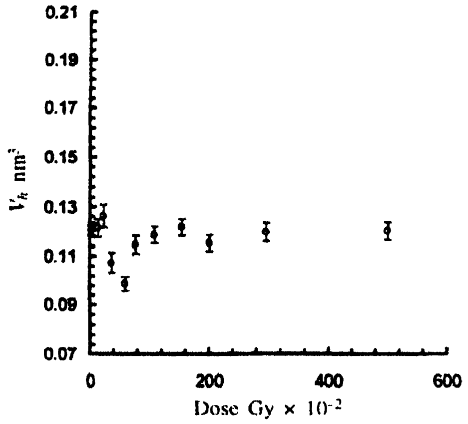

Figure 4. V_h for PE as a function of n-dose.

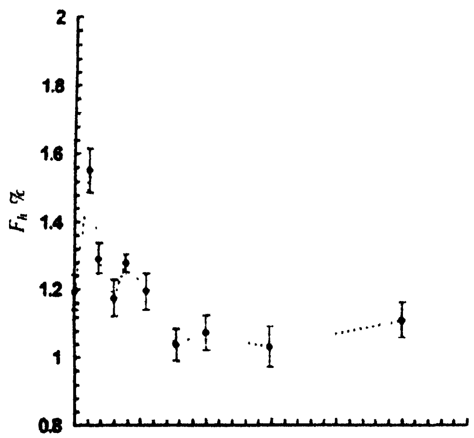

Figure 5. F_h% for PE as a function of n-dose

These results suggest degradation as the predominant process. As the neutron dose increases above 154.28×10^{-2} Gy, V_h and F_h values fluctuate, then reach their final values of 0.12 and 1.05%, respectively, corresponding to a percentage reduction of 0.98 in V_h and a percentage increment of 4.5 in F_h. Corresponding to percent increments of 21.66 and 10.35, respectively in V_h and F_h values, relative to their minimum values. The resultant reduction induced by the final n-dose in V_h value is 0.195%/Gy and an increment of 0.895%/Gy in F_h value. That implies that Ps lifetime is shortened but its intensity is increased.

Comparing the results of the n-irradiation effects on PE and PTFE microstructure, the following remarks are concluded :

1. The percentage increment in the average value of V_h is 1.3 for the irradiation PTFE samples corresponding to a percentage reduction of 3.73 in PE samples. This result suggesting the predominant of degradation in PTFE chains, whereas cross-linking is the predominance process in PE due to n-irradiation effects.
2. The percentage increment per Gray in the average value of V_h is 0.27 for PTFE, corresponding to a percentage reduction of 0.744 in PE. That means the effect of n-irradiation in the average value of V_h for PE samples is 2.76 times higher than that for PTFE samples.
3. The value of F_h for the irradiated PTFE and PE samples are 1.194% and 1.055%, respectively corresponding to percentage increment of 0.146 and 4.336, respectively. That means the increment in the average value of F_h for PE samples is 29.8 higher than that for PTFE.
4. The percentage increments in F_h per Gray are 0.029 and 0.865 for PTFE and PE, respectively.

4. Conclusion

The present results give an evidence, that PAL method can be sensitively employed as a microprobe to monitor the chemical microstructure changes of the polymer under study Present work has studied the effects of n-irradiation, thereby determining the specific dose to be used to enhance or degrade a physical property of the studied polymer.

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